

Prepared for:
United States Environmental Protection Agency
Boston, MA

Evaluation of potential causes of aluminum-impairment in 21 New Hampshire Ponds

ENSR Corporation
June 2007
Document No.: 09090-107-200D

Prepared for:
United States Environmental Protection Agency
Boston, MA

Evaluation of potential causes of aluminum-impairment in 21 New Hampshire Ponds.

David F. Mitchell

Prepared By

Don Kuhn

Reviewed By

ENSR Corporation
June 2007
Document No.: 09090-107-200D

Contents

| | |
|--|------------|
| 1.0 Introduction..... | 1-1 |
| 1.1 Aluminum Aqueous Chemistry and Toxicity | 1-1 |
| 1.2 Natural Aluminum Sources and Sinks and Anthropogenic Alteration..... | 1-3 |
| 2.0 Differentiating natural and anthropogenic sources of aluminum | 2-1 |
| 3.0 Evaluation of Aluminum-Impaired Ponds..... | 3-1 |
| 4.0 Implications for NH Aluminum TMDL Process | 4-1 |
| 5.0 Summary and Conclusions | 5-1 |
| 6.0 References | 6-1 |

Appendix A: Abstracts of Peer-Reviewed Literature on Sources of Aluminum in Watersheds and Related Topics.

List of Figures

| | |
|--|------------|
| Figure 1. Study of Aluminum-Impaired Lakes New Hampshire 2007 | 1-2 |
| Figure 2. Aluminum vs. pH for Aluminum-Impaired Lakes..... | 3-3 |
| Figure 3. Aluminum vs. Apparent Color for Aluminum-Impaired Lakes | 3-4 |
| Figure 4. Aluminum vs. Gran ANC for Aluminum-Impaired Lakes..... | 3-5 |
| Figure 5. Aluminum vs. Critical Load for Aluminum-Impaired Lakes | 3-6 |
| Figure 6. Aluminum vs. Chloride for Aluminum-Impaired Lakes | 3-7 |
| Figure 7. Aluminum vs. % Wetlands for Aluminum-Impaired Lakes..... | 3-8 |

Executive Summary

This literature report was conducted under ENSR Corporation's (ENSR) tasks under its United States Environmental Protection Agency (USEPA) contract CWQ-003 entitled "New Hampshire Total Maximum Daily Load (TMDL) Development" as part of the investigation of 21 aluminum-impaired ponds. The locations of the 21 aluminum-impaired ponds are shown on Figure 1. The source(s) of high levels of aluminum found in these ponds has been somewhat puzzling and, for purposes of TMDL allocation, it is desirable to distinguish, if possible, between natural and anthropogenic sources of aluminum. ENSR conducted this literature review to help identify potential methods of differentiating between natural and anthropogenic aluminum sources.

Section 1.0 provides an overview of aluminum aqueous chemistry and toxicity and a description of aluminum sources and sinks in watersheds and the role of anthropogenic acidification. Aluminum chemistry is very complex and environmental conditions, particularly pH and dissolved organic carbon (DOC), can favor diverse aluminum fractions that vary widely in their bioavailability and toxicity. Further details and information are available in several recent reviews (e.g., Sparling and Lowe, 1996; Gensemer and Playle, 1999; Yokel, 2004; and Ščančar and Milačič, 2006). Copies of abstracts from peer-reviewed articles which were consulted for this review are included in Appendix A.

Section 2.0 highlights recent studies that attempt to differentiate natural and anthropogenic sources of aluminum in watersheds. Models developed for northeastern United States streams and lakes have identified potentially important water chemistry and watershed characteristics that aid in the prediction of surface water aluminum concentrations. Models by Bishop et al. (2000), Palmer et al. (2005), Cory et al. (2006), and others provide promise for helping to distinguish between natural and anthropogenically-driven aluminum inputs.

Section 3.0 uses some of the concepts developed in Section 2.0 and the available water chemistry and watershed data to attempt to correlate aluminum levels with some of the attributes that have been identified as potential drivers of aluminum mobility. Comparison of aluminum levels in the 21 aluminum-impaired ponds with pH, color, acid neutralizing capacity (ANC), critical loads of acidity ($[CL_{ac}]$), the percent of the watershed in wetlands (%wetlands) and chloride were investigated (Figures 2-7). The lack of significant correlation indicates these factors do not explain the range and level of aluminum seen in the ponds.

The implications of the data analysis for the overall NH TMDL process are discussed in Section 4.0 which concludes that the influence or magnitude of natural background (the influence of organic acids in DOC fractions) is not significantly correlated with aluminum levels. Accordingly, at this time, it was conservatively concluded that the major source of aluminum is the atmospheric deposition.

A brief summary and conclusions of the report is provided in Section 5.0. Literature references and citations are provided in Section 6.0.

1.0 Introduction

This literature report is presented as part of ENSR Corporation's (ENSR) tasks under its United States Environmental Protection Agency (USEPA) contract CWQ-003 entitled "New Hampshire Total Maximum Daily Load (TMDL) Development." ENSR is providing technical support to USEPA and the New Hampshire Department of Environmental Services (NHDES) in the development of TMDL for nutrient and acid-impaired waterbodies, as part of that state's Clean Water Act Section 303(d) compliance.

A number of New Hampshire waterbodies (both ponds and rivers) have been identified as acid-impaired due to low pH readings (e.g., NHDES, 2004). A further subset of the acid-impaired waterbodies (i.e., 21 ponds) has also been identified as not meeting the state water quality criterion for aluminum (Figure 1). High aluminum concentrations in New Hampshire water bodies raise concern because of the potential toxic effects that element can have on aquatic organisms under conditions of low pH and acid-neutralizing capacity (ANC).

The source(s) of high levels of aluminum found in these ponds has been somewhat puzzling and, for purposes of TMDL allocation, it is desirable to distinguish, if possible, between natural and anthropogenic sources of aluminum. Elevated aluminum levels in aquatic systems have long been associated with acid deposition (Schindler, 1988), but the presence of natural organic acids complicates the relationship between elevated aluminum and anthropogenic acid deposition. As part of the TMDL contract, ENSR was tasked with conducting a literature review to help identify potential methods of differentiating between natural and anthropogenic aluminum sources.

The literature review provides background on current theories and potential methods of identifying the source of aluminum impairment in New Hampshire waters. We do not attempt to cover the considerable scientific literature on aluminum chemistry but have identified a number of peer-reviewed papers that provide an updated overview on the subject with particular emphasis on potential sources of aluminum. Copies of abstracts from these peer-reviewed articles are included in Appendix A. While the primary focus is on aluminum impairment of ponds, lakes, and impoundments (i.e., lentic waters), there is also concern regarding aluminum impairment of several of New Hampshire rivers and streams (i.e., lotic waters) which will be considered separately as another task of ENSR's TMDL project. For purposes of this TMDL document, ponds, lakes, and impoundments are collectively referred to as ponds.

The report is organized as follows. Section 1.1 provides an overview of aluminum aqueous chemistry and toxicity. Since aluminum chemistry and bioavailability are very complex, we have only provided the reader with an overview of the topic and leave it to the reader to refer to any of the several excellent reviews that are cited (e.g., Sparling and Lowe, 1996; Gensemer and Playle, 1999; Ščančar and Milačič, 2006). Section 1.2 describes aluminum sources and sinks in watersheds and the role of anthropogenic acidification. Section 2.0 highlights recent studies that attempt to differentiate natural and anthropogenic sources of aluminum in watersheds. Section 3.0 reviews the available data for the aluminum-impaired ponds and attempts to correlate aluminum levels with some of the pond or watershed attributes that have been identified as potential drivers of aluminum mobility. Implications of the results for the NH TMDL process are discussed in Section 4.0. A brief summary and conclusions are provided in Section 5.0. References are contained in Section 6.0.

1.1 Aluminum Aqueous Chemistry and Toxicity




Aluminum is one of the most ubiquitous elements found in nature. Aluminum is the third most abundant element on earth, but most forms are bound in primary and secondary minerals that are highly insoluble (Exley, 2006, Ščančar and Milačič, 2006). In nature, aluminum is typically found in chemical compounds with other elements such as sulfur, silicon, and oxygen.

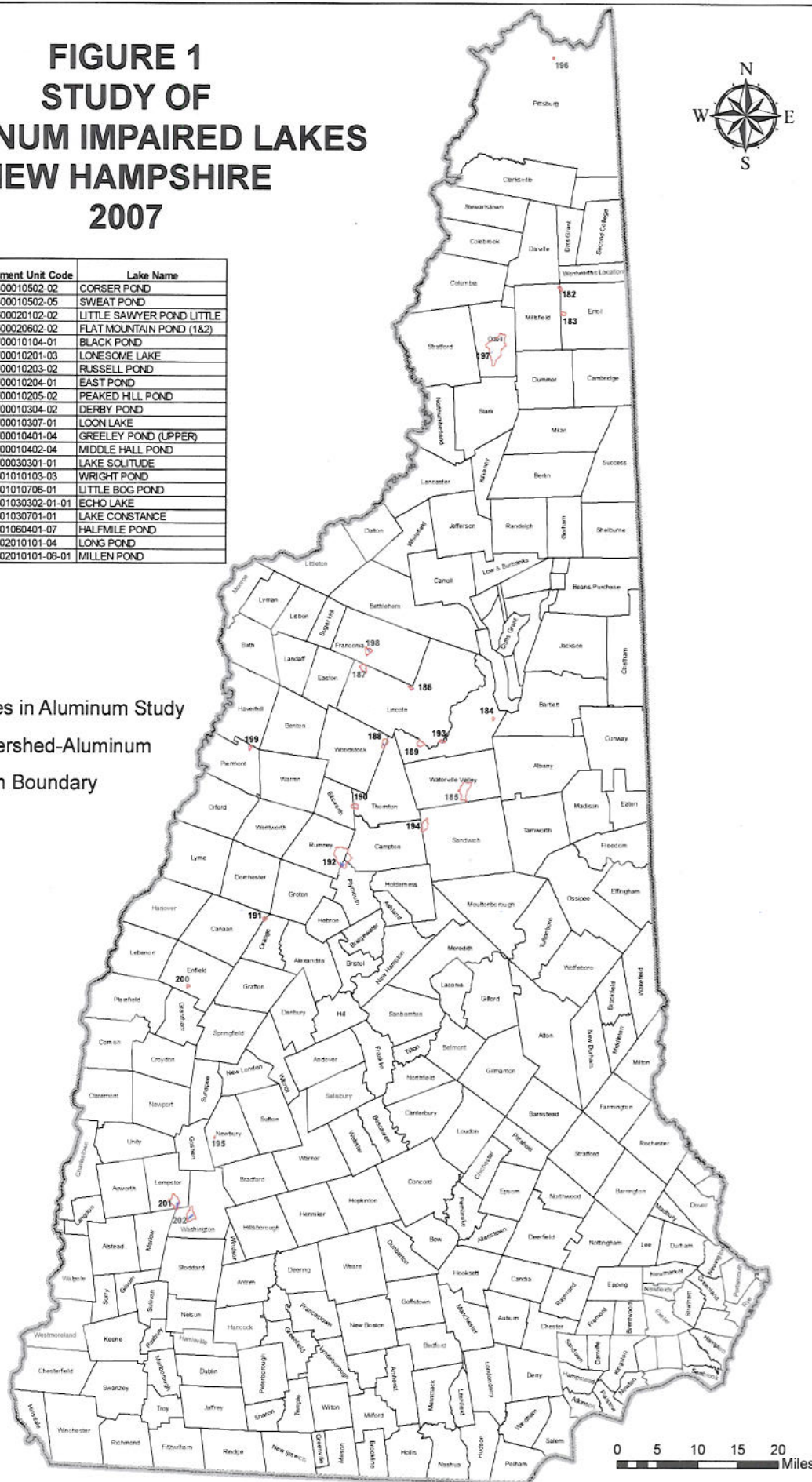
FIGURE 1 STUDY OF ALUMINUM IMPAIRED LAKES NEW HAMPSHIRE 2007



| TMDL Code | Assessment Unit Code | Lake Name |
|-----------|-----------------------|---------------------------|
| 182 | NH-LAK400010502-02 | CORSEY POND |
| 183 | NH-LAK400010502-05 | SWEAT POND |
| 184 | NH-LAK600020102-02 | LITTLE SAWYER POND LITTLE |
| 185 | NH-LAK600020602-02 | FLAT MOUNTAIN POND (1&2) |
| 186 | NH-LAK700010104-01 | BLACK POND |
| 187 | NH-LAK700010201-03 | LONESOME LAKE |
| 188 | NH-LAK700010203-02 | RUSSELL POND |
| 189 | NH-LAK700010204-01 | EAST POND |
| 190 | NH-LAK700010205-02 | PEAKED HILL POND |
| 191 | NH-LAK700010304-02 | DERBY POND |
| 192 | NH-LAK700010307-01 | LOON LAKE |
| 193 | NH-LAK700010401-04 | GREELEY POND (UPPER) |
| 194 | NH-LAK700010402-04 | MIDDLE HALL POND |
| 195 | NH-LAK700030301-01 | LAKE SOLITUDE |
| 196 | NH-LAK801010103-03 | WRIGHT POND |
| 197 | NH-LAK801010706-01 | LITTLE BOG POND |
| 198 | NH-LAK801030302-01-01 | ECHO LAKE |
| 199 | NH-LAK801030701-01 | LAKE CONSTANCE |
| 200 | NH-LAK801060401-07 | HALF MILE POND |
| 201 | NH-LAK802010101-04 | LONG POND |
| 202 | NH-LAK802010101-06-01 | MILLEN POND |

Legend

-  Lakes in Aluminum Study
-  Watershed-Aluminum
-  Town Boundary



Aluminum/pH Correlation Assessment
Development of Total Maximum Daily Loads (TMDL)
New Hampshire
Project No. EPA-SMP-07-002

171 Daniel Webster Highway, Suite 11
Belmont, New Hampshire 03220
ph: (603) 524-8866
www.ensr.aecom.com

ENSR AECOM

Proj# 09090-107
April 2007

Aluminum in ecosystems originates primarily from mineral weathering processes and biological cycling. In the northeastern United States, aluminum adsorbs to soil particles via dissolution of secondary minerals, such as silicates (Palmer et al., 2005). Relatively small amounts of aluminum become available through mineral weathering. Decaying organic matter also contributes aluminum to the exchangeable pool between soil, water, and biota in the ecosystem (Gensemer and Playle, 1999).

The concentration of aluminum in ecosystem soils and water largely depends on pH because aluminum solubility increases in acidic ($\text{pH} < 6$) and alkaline ($\text{pH} > 8$) conditions (Gensemer and Playle, 1999). Aluminum is amphoteric and can react with mineral acids to form soluble salts and to evolve hydrogen. Aluminum solubility also increases at lower temperatures and in the presence of ligands, such as humic and fulvic acids. Due to its high reactivity, aluminum is rarely found as a pure metal and it rapidly complexes to form inorganic and organic species (Ščančar and Milačič, 2006). Monomeric hydroxyl aluminum, referred to as inorganic monomeric aluminum (Al_{IM}) is the predominant inorganic aqueous species found in watersheds. Decaying organic matter generates dissolved organic carbon (DOC) that consists of organic ligands such as humic and fulvic acids that bind aluminum into organic forms.

Like aluminum solubility, aluminum speciation is primarily controlled by pH. At $\text{pH} < 5$, the inorganic monomeric aluminum (Al_{IM}) species, Al^{+3} , is most prevalent and as pH increases aluminum instantaneously transforms into other inorganic forms (Ščančar and Milačič, 2006). Changes in pH also drive the prevalence of organic monomeric Al species (Al_{OM}). However, Al_{OM} species do not respond as quickly to pH changes as Al_{IM} and this may explain the observed weaker relationship between pH and Al_{OM} compared to pH and Al_{IM} in some streams (Lydersen et al., 2002).

Speciation and pH also influences the potential toxicity to aquatic organisms. The Al_{IM} fractions are most acutely toxic for aquatic organisms (Lydersen et al., 2002), while Al_{OM} has been shown to have very little adverse effect. In acidic waters, Al_{IM} can cause acute mortality by interrupting ion-regulation in the gills of fish, causing hypoxia and has similar effects to some gilled macroinvertebrates (Gensemer and Playle, 1999). Studies suggest that Al_{IM} may be most toxic for algae at $\text{pH} \sim 6$ and is incrementally less toxic at lower pH, but more study is necessary to establish this (Passy, 2006; Gensemer and Playle, 1999). Greater detail of aluminum speciation and toxicity can be found in Gensemer and Playle (1999), Lydersen et al. (2002), Yokel (2004), and Ščančar and Milačič (2006). [Note: Copies of abstracts from peer-reviewed articles are included in Appendix A].

1.2 Natural Aluminum Sources and Sinks and Anthropogenic Alteration

The mechanisms controlling aluminum concentration and speciation also determine the sources and sinks of aqueous aluminum. Aluminum is naturally present throughout ecosystems and can be controlled by natural acids. Humans often alter aluminum equilibrium into ecosystems by acidifying water bodies through atmospheric pollution or acid mine drainage (Driscoll et al., 2003). Hence, identifying sources and movement of aluminum in watersheds is integral to identifying as well as controlling or mitigating anthropogenic-induced aluminum impairment.

Watershed soils serve as a natural source of aluminum in water bodies due to the accumulation of aluminum from mineralization and the decay of organic material in the upper organic soil horizons, or O horizon. Aluminum adsorbed on mineral soil particles can then be transported into streams through soil water movement (interflow) during precipitation and snowmelt events (Cory et al., 2006). Pellerin et al. (2002) found evidence of aluminum movement from watershed upland soils to riparian areas in the Bear Brook Watershed of Maine. They found concentrations of inorganic and organic aluminum in the O horizon adjacent to the stream were greater than concentrations of upslope O horizons suggesting mass transfer through groundwater or overland flow.

Wetlands can serve as both potential sources and sinks of aluminum in watersheds due to the influence of organic acid derived from decomposition of peat and woody debris. Wetlands generate considerable amounts

of DOC that can bind aluminum and reduce its inherent toxicity. Wetlands, particularly riparian wetlands, can therefore serve as an aluminum sink (Yavitt et al., 2006). However, wetlands can also export DOC and introduce Al_{OM} into a water body (Gorham et al., 1998). This results in a typically strong positive relationship between Al_{OM} and DOC in freshwaters (Palmer et al., 2005). In addition to binding aluminum, strong organic acids generated by DOC can lower pH and increase the solubility of Al_{IM} in waters (Munsen and Gherini, 1993; Lawrence et al., 2007). This suggests that natural acidity may mobilize Al_{IM} and result in lowered pH which shifts the aluminum toward more toxic forms. However, Lawrence et al. (2007) indicated that the presence of strong organic acids would not mobilize Al_{IM} if there were adequate buffering capacity as was found in the high DOC streams in the Adirondacks of New York.

Acid deposition introduces strong inorganic acids into watersheds and consequently alters the equilibrium of aluminum in water bodies. Elevated aluminum concentrations originate from the same natural sources, but tend to increase the flux of inorganic aluminum in waters from mineral soils in the watershed (Cory et al., 2006). Aluminum concentrations in soils increase in these acidified waters as a result of enhanced solubility. Aluminum ions attach to soil cation exchange sites after cations, such as Ca^{2+} and Mg^{2+} , have been stripped by hydrogen ions (H^+) and other strong acids from the soil. As soils become saturated with aluminum, larger concentrations are transported to streams and lakes during acidic rain or snowmelt events (Adams et al., 2006).

Aluminum mobilized from mineral soils is typically Al_{IM} due to the absence of organic ligands; although some organic species may be mobilized from soil organic matter. Taking this into account as well as the fact that Al_{IM} is the most toxic form for aquatic life, Lawrence et al. (2007) suggested that the presence of Al_{IM} in water bodies is indicative of anthropogenic impairment. The role of natural acids in mobilization of Al_{IM} is only beginning to be researched, but they appear to be a minor factor driving Al_{IM} mobilization compared to strong inorganic acids introduced by anthropogenic inputs.

2.0 Differentiating natural and anthropogenic sources of aluminum

Due to the complexity that wetlands and natural acidity adds to differentiating sources of aluminum impairment, various models and categorization techniques are beginning to be developed in order to assist in identifying natural and anthropogenic components. These models are beginning to revise the previously simple model of aluminum mobilization solely by atmospheric deposition. At this point, however, no strong consensus has emerged regarding the best paradigm to use.

Models developed for northeastern United States streams and lakes have identified potentially important watershed characteristics that aid in the prediction of surface water aluminum concentrations (see Appendix A). Palmer et al. (2005) modeled aluminum and DOC in the Hubbard Brook, NH watershed based on soil characteristics. The study identified hydrologic flowpaths and residence times as potentially influential landscape characteristics. Streams with the greatest total aluminum concentrations had shallow hydrologic flowpaths and short residence times. However, streams with deep organic soils and hence long hydrologic flow paths also had high aluminum concentrations. The high concentrations of DOC in the streams with a greater influence of deep organic soils suggested that the aluminum contained a higher percentage of Al_{OM} . Ito et al. (2005) similarly found the highest annual flux of aluminum into Adirondack lakes of New York was associated with lakes with thin till soils in sub-watersheds. Lakes with highest average DOC had the highest concentration of monomeric aluminum than those without, but the exact speciation was not indicated.

In addition to predicting aluminum concentration from landscape characteristics, models have been developed in Sweden to estimate the anthropogenic component using aluminum speciation. Bishop et al., (2000) proposed the Boreal Dilution Model to separate natural and anthropogenic components of pH decline in boreal streams impaired by episodic acidification. Episodic acidification is a short-term decline in ANC to less than zero and pH to below 6 that occurs in streams during acidic storm-events and snowmelt (Wigington et al., 1996). The model uses base flow stream chemistry as the baseline for natural conditions and estimates the effect of base cation dilution, organic acids, and strong inorganic acids from acid deposition on pH during a storm event. This is used to predict the low pH conditions (often worst case for aquatic receptors) associated with spring runoff-snowmelt conditions.

Building upon the Boreal Dilution Model, Cory et al. (2006) predicted the anthropogenic component of aluminum increase in streams during episodic acidification. The study determined that the factors of greatest significance to aluminum concentration and speciation were landscape type (% of wetland area in the sub-watershed), stream pH and DOC. The Swedish streams were classified by wetland land cover in sub-watersheds. As anticipated, streams with the largest percentage of wetlands in their sub-watershed had a lower average Al_{IM}/Al_{total} ratio due to the domination of Al_{OM} . Using the average Al_{IM}/Al_{total} ratio and the relationship between pH and Al in the each stream category, Cory et al. (2006) estimated the portion of Al_{IM} increase linked with the estimated anthropogenic pH decline from Boreal Dilution Model results.

These models and classification techniques require further validation, but provide a potential basis on which to determine the source of aluminum impairment in New Hampshire ponds and streams. Accordingly, some of these concepts were further investigated using water chemistry and watershed data from the aluminum-impaired ponds of interest (see Section 3.0).

3.0 Evaluation of Aluminum-Impaired Ponds

As indicated in Section 2.0, some recent studies suggest that aluminum levels are potentially linked to pond water quality parameters or watershed characteristics (Palmer et al., 2005; Ito et al., 2005; Cory et al., 2006). We examined the water chemistry and watershed characteristics of the 21 aluminum-impaired ponds to see if these relationships held and/or provided insight into attributing levels of aluminum to either natural or anthropogenic sources for purposes of TMDL development. These water quality parameters included pH, color (used as a surrogate for DOC), and chloride, as well as the composite values of acid neutralizing capacity (gran ANC) and the annual critical loading ($[CL_{ac}]$) factor (Henriksen and Posch, 2001). In addition, the percentage of wetlands (% wetlands) in the watershed was considered.

The rationales for selection of these parameters were as follows – pH and color were used since both have been shown to influence the amount of aluminum mobilized. Lower values of pH are associated with higher values of soluble (free) aluminum due to its amphoteric nature. DOC may also influence aluminum mobility, but its influence is harder to predict. We did not have DOC values for the 21 ponds but used color as a surrogate parameter since color of a pond is usually highly related to the DOC content (Pace and Cole, 2002).

The gran ANC and $[CL_{ac}]$ values were used as indicators of the relative magnitude of atmospheric deposition – the lower these values (or more negative) the less the ability of the pond to offset the effects of mineral acid inputs, the higher the expected aluminum levels. Chloride was used as an indirect indicator of anthropogenic influence because higher levels of chloride are often associated with watershed development and impervious areas due to road salt and other applied materials (e.g., fertilizers). As indicated by Figure 1, the aluminum-impaired watersheds are not located near the ocean so that maritime-derived salts should not be a factor. Finally, the % wetlands in a watershed has been shown to be an important determinant of aluminum availability because of the introduction of organic acids (Cory et al., 2006).

The locations of the 21 aluminum-impaired ponds are shown in Figure 1 which also includes a list of the ponds. Water chemistry data for the aluminum-impaired ponds were obtained from the NHDES Environmental Monitoring Database. Data were preferentially obtained from 1996-2007, but data for some parameters for select ponds were not always available from this time period. In these instances, data from 1991-1995 were used instead. An arithmetic mean was calculated for each water quality parameter for each lake. The resulting means were used in the regression analysis.

Annual $[CL_{ac}]$ values were calculated using watershed runoff and mean concentrations of base cations and mineral acids, all corrected for the influence of sea salt (for details on the determination of $[CL_{ac}]$ values refer to Henriksen and Posch (2001) or Henriksen, Dillon, and Aherne. (2002).

The percentage of wetlands in the watershed was determined by summing the wetland area (as determined by the U.S. Fish and Wildlife National Wetlands Inventory data taken from the 1:24,000 scale topographic maps digitized by NH GRANIT) and comparing this to total watershed area. For purposes of this calculation, we eliminated the actual pond areas (i.e., areas identified as L1UB and PUBH codes) from the total wetlands/watershed assessment.

The relationship between total aluminum concentrations and the water quality parameters were analyzed for trends and statistical relevancy using simple linear and polynomial regressions (Figures 2-6), although statistical significance (p-value) was only calculated for the linear regression. There were no strong or significant relationships between aluminum and any of the water quality parameters assessed. The lack of significant correlation for pH (Figure 2), color (Figure 3), gran ANC (Figure 4) and $[CL_{ac}]$ (Figure 5) suggests these factors do not explain the range and level of aluminum seen in the ponds.

The use of surrogate indicators for watershed development including chloride (Figure 6) and % wetland (Figure 7) are equally poor predictors. Chloride data from the 21 ponds tended to be very much skewed to low values and are not suitable for regression. Also, as indicated in Figure 1, these low chloride levels may have been expected from the rather remote central location of the pond watersheds away from centers of population. Finally, the % wetlands was not a good predictor, but we note that the range of percentages (<1 % - 3.5%) is very limited and only occupies a small portion of the range of percentage classes (i.e., from <1 to 40%) used in the Cory et al. (2006) paper. It should be noted that most of the aluminum-impaired ponds are remote, high-elevation waterbodies, with similar watershed characteristics including small size and shallow depth to bedrock, and are represented by water quality samples collected once yearly (late spring). The similarity of the watershed/pond settings is likely to reduce the ability of the existing data set to distinguish potential trends between aluminum and potential causal factors.

The failure to find meaningful relationships in the available New Hampshire data set between aluminum and water chemistry or watershed characteristics for the 21 ponds does not mean that such relationships may not exist. The reliance on total aluminum concentrations may mask potential influence of these factors. For example, a relationship between these water quality and watershed parameters and selected fractions of aluminum (e.g., Al_{IM}) may exist. This would be of importance since it would provide a more useful index of potential toxicity to sensitive aquatic receptors. Further investigation would be required to fully evaluate these potential relationships and could include: (1) measurement of water chemistry (pH, ANC, DOC) and aluminum fractions (total and dissolved, Al_{IM} , Al_{OM} , etc.); and (3) re-examination of the relationship with % wetlands in a watershed over a larger range of percentiles. Other potential avenues of inquiry include further characterization of aluminum fractions with regard to watershed soils, the nature and depth of soils in watersheds and/or hydrologic flowpath combinations. Recent research on the interaction among pH, DOC, and aluminum levels in relation to toxicity to juvenile Atlantic salmon in eastern Maine rivers may also shed light on the subject (NOAA and MASC, 2006).

Based on the current data set, the lack of correlation of aluminum with the water chemistry data or watershed characteristics does not conclusively define the nature or the source of aluminum impairment in New Hampshire ponds and streams. However, the lack of a discernible relationship of aluminum levels with either color or the % wetland in the watershed does not support the theory of a strong natural source of aluminum due to organic acids. With the present data and understanding of the field, the most likely explanation may be that the major source of aluminum impairment is due to the anthropogenic influence of atmospheric deposition.

Figure 2. Al vs pH for Aluminum Impaired Lakes

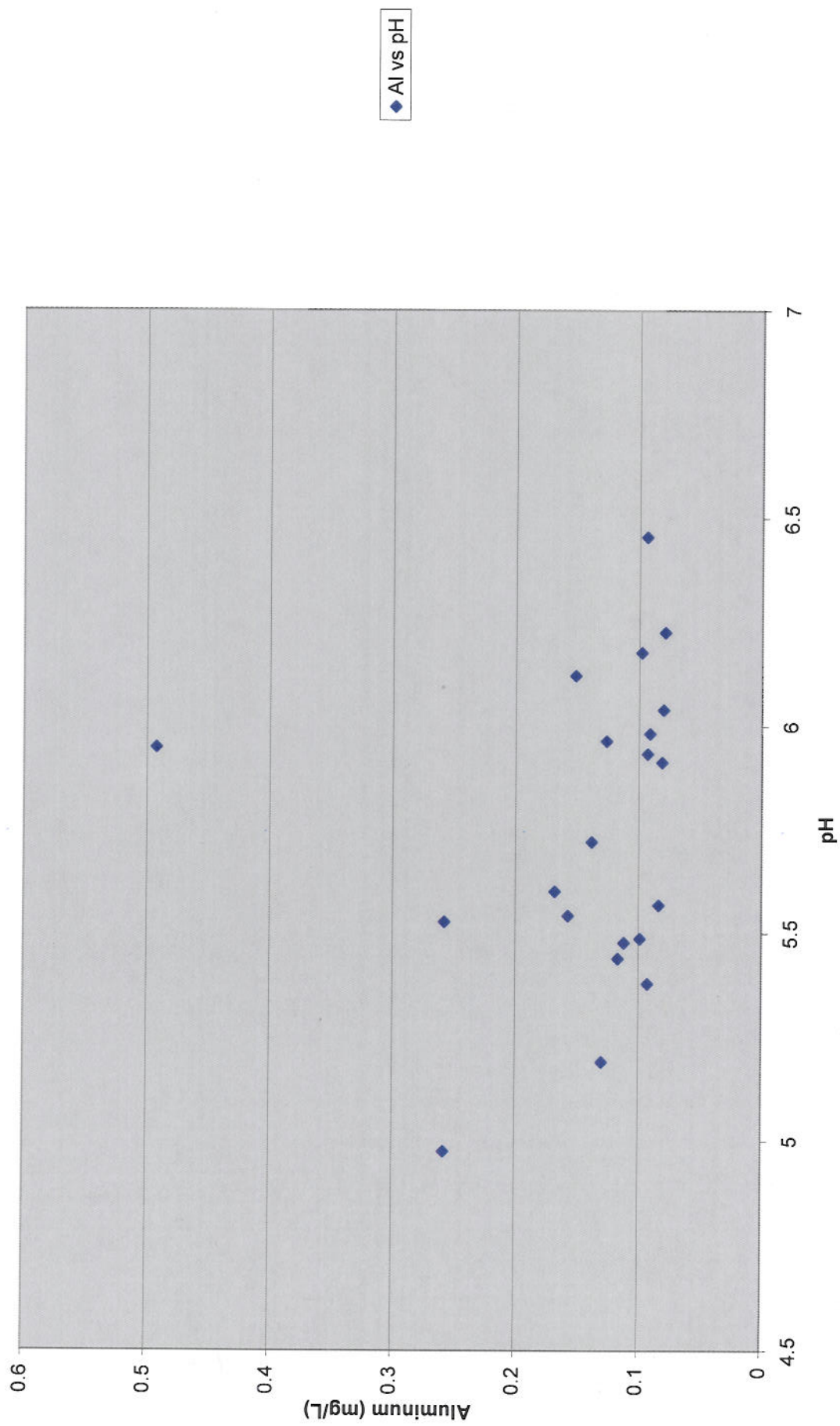


Figure 3. Al vs Apparent Color for Aluminum Impaired Lakes

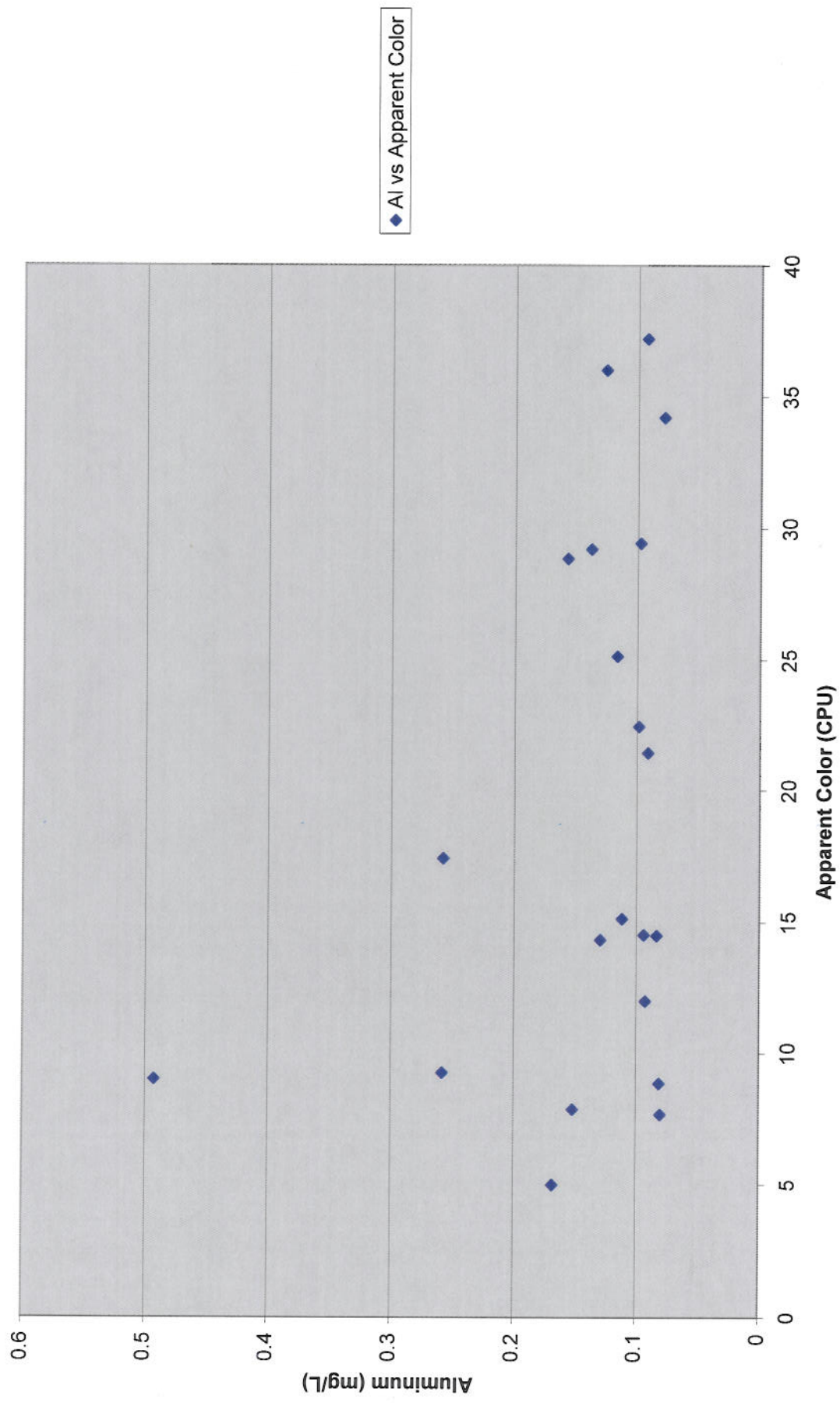


Figure 4. Al vs Gran ANC for Aluminum Impaired Lakes

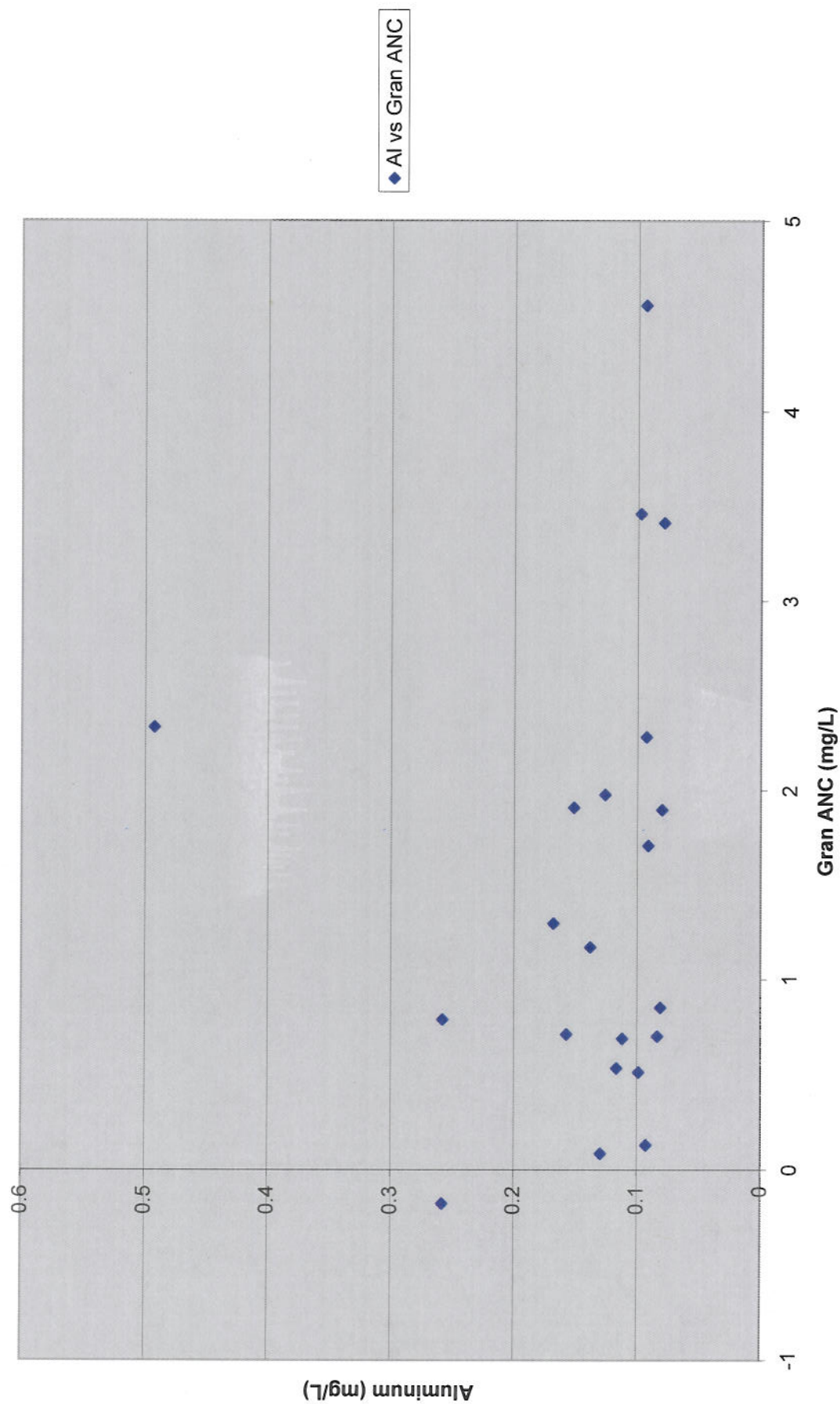


Figure 5. Al vs Critical Load for Acid Impairment

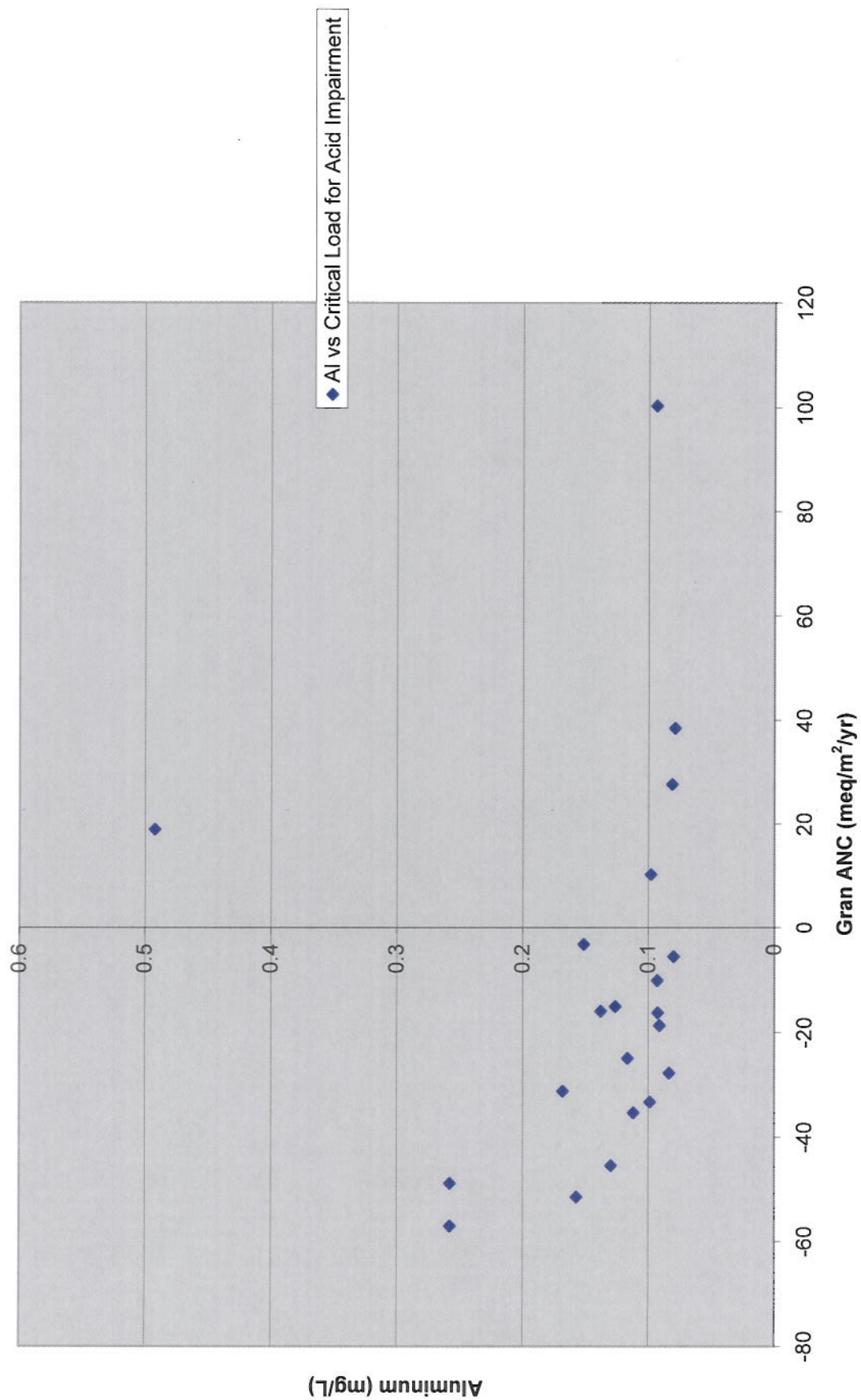


Figure 6. Al vs Chloride for Aluminum Impaired Lakes

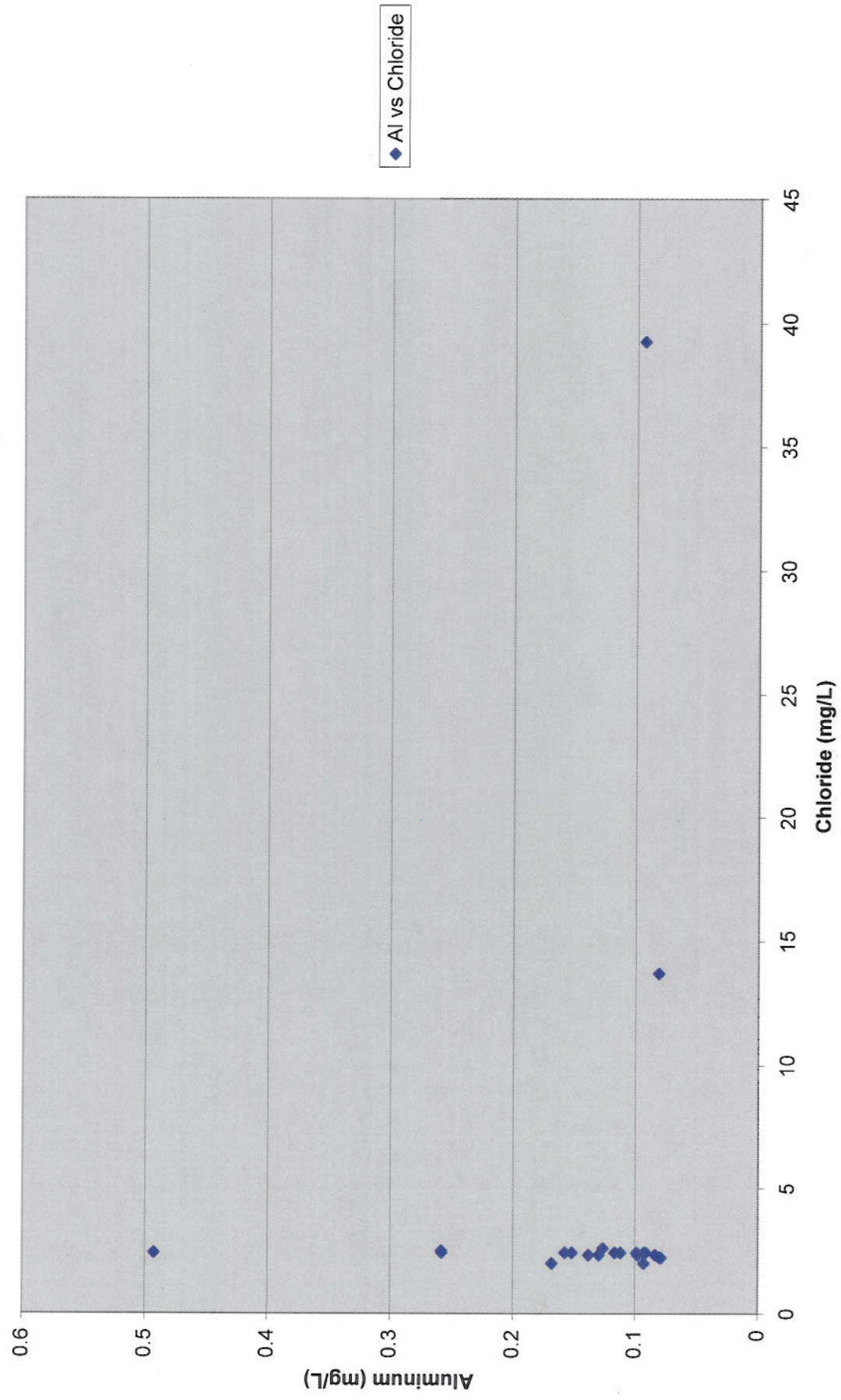
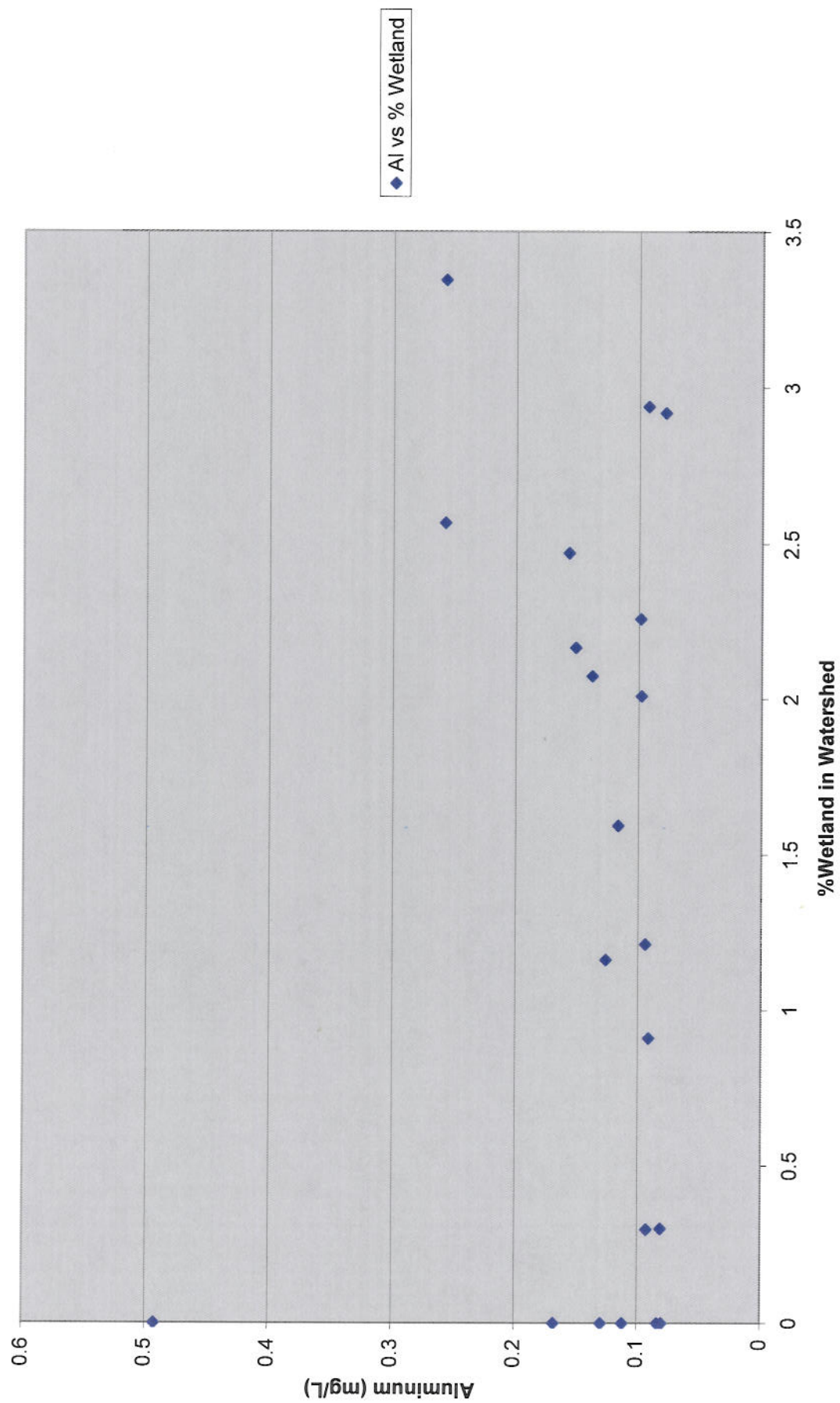


Figure 7. Al vs %Wetland for Aluminum Impaired Lakes



4.0 Implications for NH Aluminum TMDL Process

According to the 40 CFR Part 130.2, the TMDL for a waterbody is equal to the sum of the individual loads from point sources (i.e., wasteload allocations or WLAs), and load allocations (LAs) from nonpoint sources (including natural background conditions). Section 303(d) of the CWA also states that the TMDL must be established at a level necessary to implement the applicable water quality standards with seasonal variations and a margin of safety (MOS) which takes into account any lack of knowledge concerning the relationship between effluent limitations and water quality. In equation form, a TMDL may be expressed as follows:

$$\text{TMDL} = \text{WLA} + \text{LA} + \text{MOS}$$

where:

WLA = Waste Load Allocation (i.e., loadings from point sources);

LA = Load Allocation (i.e., loadings from nonpoint sources including natural background

MOS = Margin of Safety.

New Hampshire has placed restrictions on the discharge of wastewater treatment or industrial facilities to lacustrine environments, preferring to direct such discharges into riverine environments. Therefore, with regard to the WLA term, there are no known point sources (i.e., permitted discharges) of aluminum discharging to the ponds evaluated in this TMDL nor are they present in their watersheds. This term is accordingly defined as zero.

The LA term represents the aluminum load derived from nonpoint sources including natural background. While the actual source of the aluminum is weathering and mobilization of bedrock and organic materials by acidic inputs to the watershed, the ultimate "load" of concern is the acid components themselves and how they are divided into anthropogenic sources (strong inorganic acids derived from atmospheric deposition) or natural background (organic acids arising from decomposition).

Based on the discussion presented in Section 3.0, the influence or magnitude of natural background (the influence of organic acids in DOC fractions) is not significantly correlated with aluminum levels. Accordingly, at this time, it must be conservatively concluded that the major source of aluminum is the soil and rock dissolution by atmospheric deposition of acids. This is the same primary causal factor that is responsible for the low pH values currently seen in the water quality data of New Hampshire's acid-impaired ponds. Therefore, it is appropriate that both pH and aluminum issues should be concurrently addressed within the acid pond TMDL development.

5.0 Summary and Conclusions

This literature report was conducted as part of the investigation of aluminum-impaired ponds and to help identify potential methods of differentiating between natural and anthropogenic aluminum sources. Aluminum chemistry and its interaction with environmental factors is an important and active research field. The accepted paradigm of aluminum loadings to low pH waters controlled largely by atmospheric deposition is giving way to the acknowledgment of the complex role played by organic acids in influencing the amounts, seasonality, and toxicity of aluminum in New England waters.

While the research efforts are promising, extrapolation of these theories to look for simple relationships between aluminum and potential causal factors that distinguish between natural and anthropogenic sources did not prove successful. There are likely several reasons why these analyses should not be considered definitive, including, but not limited to: small size of the database, lack of aluminum fraction data, similarity in watershed/pond settings, and diversity in the time of year that data was collected. Further work to reduce this uncertainty may be conducted, but may or may not result in useful predictive models. Even if predictive models are generated, it is doubtful these would result in direct application to TMDL implementation efforts for purposes of mitigating aluminum impairment in New Hampshire waters, since it has been recognized that the bulk of the causal acidifying pollutants contributing to this impairments are from sources well beyond New Hampshire's borders (USEPA, 2003; Kahl et al., 2004). Aside from participating in litigation to uphold federal requirements, New Hampshire has little direct control over these sources and is forced to rely on national enforcement efforts spearheaded by the U.S. EPA. It is expected that reduction in upwind emissions of acidifying pollutants are needed to reduce the aluminum exceedances in New Hampshire's waters. Given the iterative nature (adaptive management) of the TMDL process, this issue may be relegated to review in a future regulatory cycle.

6.0 References

- Adams, M., DeWalle, D., and J. Horn, Eds. 2006. The Fernow Watershed Acidification Study. Environmental Pollution Vol. 11. Springer, New York.
- Bishop, K., Laudon, H., Kohler, S. 2000. Separating the natural and anthropogenic components of spring flood pH decline: A method for areas that are not chronically acidified. *Water Resources Research*. 36 (7): 1873-1884.
- Cory, N., Buffam, I., Laudon, H., Kohler, S., and K. Bishop. 2006. Landscape control of stream water aluminum in a boreal catchment during spring flood. *Environ. Sci. & Technol* 40 (11): 3494-3500.
- Driscoll, C., Driscoll, K., Roy, K. and M. Mitchell. 2003. Chemical response of lakes in the Adirondack Region of New York to declines in acidic deposition. *Environ. Sci. & Technol*. 37, 2036-2042.
- Exley, C. 2003. A biogeochemical cycle for aluminum? *J. of Inorganic Biochem*. 97 (1): 1-7
- Gensemer, R. and R. Playle. 1999. The bioavailability and toxicity of aluminum in aquatic environments. *Crit. Rev. Environ. Sci. Technol*. 29:315-450.
- Gorham, E., Underwood, J., Janssens, J., Freedman, B., Maass, W., Waller, D., and J. Ogden III. 1998. The chemistry of streams in southwestern and central Nova Scotia, with particular reference to catchment vegetation and the influence of dissolved organic carbon primarily from wetlands. *Wetlands*. 18:115-132.
- Henriksen, A. and M. Posch. 2001. Steady-state models for calculating critical loads of acidity for surface waters. *Water, Air, and Soil Pollution: Focus* 1:375-398.
- Henriksen, A., Dillon, P., and J. Aherne. 2002. Critical loads of acidity for surface waters in south-central Ontario, Canada: regional application of the Steady-State Water Chemistry (SSWC) model. *Can. J. Fish Aquat. Sci*. 59:1287-1295
- Ito M., Mitchell, M., Driscoll, C., and K. Roy. 2005. Factors affecting acid neutralizing capacity in the Adirondack region of New York: A solute mass balance approach. *Environ. Sci. & Technol* 39 (11): 4076-4081.
- Kahl, J., Stoddard, J., Haeuber, R., Paulsen, S., Birnbaum, R., Deviney, F., Webb, J., DeWalle, D., Sharpe, W., Driscoll, C., Herlihy, A., Kellogg, J., Murdoch, P., Roy, K., Webster, K., and N. Urquhart. 2004. Have U.S. Surface Waters Responded to the 1990 Clean Air Act Amendments? *Environ. Sci. Technol*. 38:484A-490A.
- Lawrence, G., Sutherland, J., Boylen, C., Nierzwicki-Bauer, S., Momen, B., Baldigo, B., and H. Simonin. 2007. Acid rain effects on aluminum mobilization clarified by inclusion of strong organic acids. *Environ. Sci. & Technol* 41 (1): 93-98.
- Lydersen, E., Löfgren, S., and R. Arnesen. Metals in Scandinavian Surface Waters: Effects of Acidification, Liming, and Potential Reacidification. 2002. *Crit. Rev. Environ. Sci. Technol*. 32(2&3):73-295.
- Munson, R. and S. Gherini. 1993. Influence of organic-acids on the pH and acid-neutralizing capacity of Adirondack Lakes. *Water Resource Res*. 29 (4): 891-899.

- New Hampshire Department of Environmental Services. 2004. *Total Maximum Daily Load (TMDL) for 65 Acid Impaired New Hampshire Ponds. Final Report*. NHDES, Concord, NH.
- National Oceanic and Atmospheric Administration (NOAA) and Maine Atlantic Salmon Commission (MASC). 2006. Effects of low pH and High aluminum on Atlantic salmon smolts in Eastern Maine and liming project feasibility analysis. U.S. Atlantic Salmon Assessment Committee Working Paper. 27 pp.
- Pace, M. and J. Cole. 2002. Synchronous variation of dissolved organic carbon and color in lakes. *Limnol. Oceanogr.* 47:333-342.
- Palmer, S., Wellington, B., Johnson, C. and C. Driscoll. 2005. Landscape influences on aluminum and dissolved organic carbon in streams draining the Hubbard Brook valley, New Hampshire, USA. *Hydrol. Process.* 19 (9): 1751-1769.
- Passy, S. 2006. Diatom community dynamics in streams of chronic and episodic acidification: The roles of environment and time. *J. Phycol.* 42:312-323.
- Pellerin, B., Fernandez, I., Norton, S., and J. Kahl. 2002. Soil aluminum distribution in the near-stream zone at the Bear Brook Watershed in Maine. *Water Air & Soil Poll.* 134 (1-4): 189-204.
- Ščančar, J and R. Milačič. 2006. Aluminum speciation in environmental samples: a review. *Anal Bioanal Chem.* 386: 999–1012.
- Schindler, D. 1988. Effects of acid-rain on fresh-water ecosystems. *Science.* 239:149-157.
- Sparling, D. and T. Lowe. 1996. Environmental hazards of aluminum to plants, invertebrates, fish, and wildlife. *Res. Environ. Contam. Toxicol.* 145:1-127.
- United States Environmental Protection Agency. 2003. Responses of surface water chemistry to the Clean Air Act Amendments of 1990. EPA-620/R-03/001.
- Wigington, P., DeWalle, D., Murdoch, P., Kretser, W., Simonin, H., VanSickle, J., and J. Baker. 1996. Episodic acidification of small streams in the northeastern United States: Ionic controls of episodes. *Ecol. Appl.* 6:389-407.
- Yavitt, J., Fahey, T., Long, R., and C. Driscoll. 2006. Solutes and soil in and around an in-stream wetland on the Hubbard Brook Experimental Forest, NH, USA. *Wetlands* 26(2): 376–384.
- Yokel RA (2004) In: Merian E., Anke, M., Ihnat, M., and M Stoeppler, (eds). Aluminum: elements and their compounds in the environment. Occurrence, analysis and biological relevance. Vol. 2. Wiley-VCH, Weinheim, Germany.

APPENDIX A

ABSTRACTS OF PEER-REVIEWED LITERATURE ON SOURCES OF ALUMINUM IN WATERSHEDS AND RELATED TOPICS

Separating the natural and anthropogenic components of spring flood pH decline: A method for areas that are not chronically acidified

WATER RESOURCES RESEARCH, VOL. 36, NO. 7, PAGES 1873–1884, JULY 2000

Kevin H. Bishop and Hjalmar Laudon

Department of Environmental Assessment, Swedish University of Agricultural Sciences, Uppsala

Stephan Kohler

Department of Forest Ecology, Swedish University of Agricultural Sciences, Umeå

Abstract.

The quantitative distinction of the natural and anthropogenic components of episodic pH decline is important but problematic. This paper presents the Boreal Dilution Model as a means of separating the natural effects of acid neutralizing capacity (ANC) dilution and organic acids from those of acid deposition on stream pH during spring flood or other flow episodes in areas that are not chronically acidified. Key model assumptions are that base flow ANC reflects preindustrial ANC, that the contemporary dissolved organic carbon is natural, and that dilution of base cations during spring flood is a measure of natural ANC dilution. The model could help elucidate the natural variation of spring flood chemistry, as well as the response to changes in acidification pressures. An example of the model's application to one catchment is presented. This example, together with the correlation between winter SO₄ 22 deposition and modeled anthropogenic ANC depression during spring flood in some 27 episodes from 18 catchments, is presented to assess the model's plausibility.

Landscape Control of Stream Water Aluminum in a Boreal Catchment during Spring Flood

NEIL CORY,*† ISHI BUFFAM,‡
HJALMAR LAUDON,§
STEPHAN KÖHLER,‡ AND KEVIN BISHOP†
*Department Environmental Assessment, Swedish University of
Agricultural Sciences, Sweden, Department Forest Ecology,
Swedish University of Agricultural Sciences, Sweden,
Department Ecology and Environmental Science,
Umeå University, Sweden, and Department Applied
Geosciences, Graz University of Technology, Austria*

Environ. Sci. Technol. 2006, 40, 3494–3500

Inorganic aluminum (Al) concentrations are critical for defining the biological effects of acidification. The landscape's role in controlling the spatial variability of Al and its speciation has received only limited attention. We analyzed the speciation of stream Al at 14 sites within a 68 km² boreal catchment during spring snowmelt, a period of episodic acidity. Three factors that influenced Al at these sites were landscape type (specifically the proportion of wetland areas), stream pH, and dissolved organic carbon (DOC). Forested catchment sites underlain by mineral soils had higher total Al concentrations and greater inorganic Al proportions than catchments with larger wetland areas, despite significantly higher pH. We suggest that this difference results from source limitation of Al in the peat wetlands. The control of Al solubility was dominated by organic complexes, with the organic carrying capacity exceeding Al in the majority of samples. When assessing the inorganic phase, only four percent of the samples were oversaturated with regards to commonly forming secondary Al minerals, with no samples showing supersaturation higher than 10 times with respect to any given solid phase. Inorganic Al rarely exceeded biological thresholds, except for short periods during peak flow in forested areas, despite two-thirds of the streams having minimum pH values below 4.9. Streams with a high percentage of wetland area were associated with lower Al:DOC ratios. The Al:DOC ratios were quite stable in each stream before, during, and after snowmelt, with the exception of isolated spikes in the Al:DOC ratio associated with particulate Al at a downstream site during high flow.

Chemical Response of Lakes in the Adirondack Region of New York to Declines in Acidic Deposition

CHARLES T. DRISCOLL, *, † KIMBERLEY M. DRISCOLL, †
KAREN M. ROY, ‡ AND MYRON J. MITCHELL §

Environ. Sci. & Technol. 37: 2036-2042.

Abstract

Long-term changes in the chemistry of wet deposition and lake water were investigated in the Adirondack Region of New York. Marked decreases in concentrations of SO_4^{2-} and H^+ in wet deposition have occurred at two sites since the late 1970s. These decreases are consistent with long-term declines in emissions of sulfur dioxide (SO_2) in the eastern United States. Changes in wet NO_3^- -deposition and nitrogen oxides (NO_x) emissions have been minor over the same interval. Virtually all Adirondack Lakes have shown marked decreases in concentrations of SO_4^{2-} , which coincide with decreases in atmospheric S-deposition. Concentrations of NO_3^- have also decreased in several Adirondack lakes. As atmospheric N deposition has not changed over this period, the mechanism contributing to this apparent increase in lake/watershed N retention is not evident. Decreases in concentrations of $\text{SO}_4^{2-} + \text{NO}_3^-$ have resulted in increases in acid neutralizing capacity (ANC) and pH and resulted in a shift in the speciation of monomeric Al from toxic inorganic species toward less toxic organic forms in some lakes. Nevertheless, many lakes continue to exhibit pH values and concentrations of inorganic monomeric Al that are critical to aquatic biota. Extrapolation of rates of ANC increase suggests that the time frame of chemical recovery of Adirondack Lakes will be several decades if current decreases in acidic deposition are maintained.

A biogeochemical cycle for aluminum?

Christopher Exley

Journal of Inorganic Biochemistry 97 (2003) 1–7

Abstract

The elaboration of biogeochemical cycles for elements which are known to be essential for life has enabled a broad appreciation of the homeostatic mechanisms which underlie element essentiality. In particular they can be used effectively to identify any part played by human activities in element cycling and to predict how such activities might impact upon the lithospheric and biospheric availability of an element in the future. The same criteria were the driving force behind the construction of a biogeochemical cycle for aluminum, a non-essential element which is a known ecotoxicant and a suspected health risk in humans. The purpose of this exercise was to examine the concept of a biogeochemical cycle for aluminum and not to review the biogeochemistry of this element. The cycle as presented is rudimentary and qualitative though, even in this nascent form, it is informative and predictive and, for these reasons alone, it is deserving of future quantification. A fully fledged biogeochemical cycle for aluminum should explain the biospheric abundance of this element and whether we should expect its (continued) active involvement in biochemical evolution.

The Bioavailability and Toxicity of Aluminum in Aquatic Environments

Robert W. Gensemer*

Department of Biology, Boston University, 5 Cummington St., Boston, MA 02215

Richard C. Playle

Department of Biology, Wilfrid Laurier University, Waterloo, Ontario, N2L 3C5,

Canada

Crit. Reviews in Environ. Sci. & Technol. (1999) 29:315-450.

ABSTRACT: In this article we review the biological effects of Al, primarily with respect to the chemical factors controlling Al bioavailability and toxicity, and how its biological effects are best predicted. Our intent is not to duplicate recent reviews on Al chemistry or toxicity, but rather to update the literature since these reviews were published, and to focus on Al speciation and other external chemical influences on Al bioavailability to freshwater biota. Briefly, we first review Al chemistry, with a specific focus on understanding, as well as measuring, Al chemical species of importance to aquatic biota. Next we more comprehensively review Al toxicity and bioavailability to freshwater algae, with a thorough analysis of the relationships between speciation and toxicity, the role of important chemical complexing agents such as P, Si, and organic carbon, as well as the potential for Al to impact algal community structure. A third section reviews the more sparse literature on aquatic higher plants; the fourth section reviews a somewhat more abundant literature of Al toxicity to freshwater invertebrates. We close with an updated review of Al toxicity to fish, again with a focus on mechanisms of toxicity, and the role of Al speciation in controlling bioavailability.

The chemistry of streams in southwestern and central Nova Scotia, with particular reference to catchment vegetation and the influence of dissolved organic carbon primarily from wetlands.

Gorham, E.; Underwood, J.K.; Janssens, J.A.; Freedman, B.; Maass, W.; Waller, D.H.; and Ogden III. J.G. 1998. Wetlands 8(1): 115-132

Abstract

The percentage of wetlands in a catchment accounted for about half of the variance in transformed data for concentrations of dissolved organic carbon (DOC) in 42 Nova Scotian streams draining catchments with 11 different kinds of vegetation. Color increased with DOC, as did total dissolved nitrogen (TDN). The color/DOC and DOC/TDN quotients also rose with increasing DOC, indicating a change in the quality of dissolved organic matter with increasing wetland influence. Dissolved Fe, and to a lesser extent dissolved Al, showed a strong positive correlation with DOC. Stream pH showed a strong negative correlation with DOC, largely from wetlands, and a strong positive correlation with non-marine Ca^{2+} weathered from mineral soils. Non-marine SO_4^{2-} from acid deposition had no apparent influence on stream pH and decreased with increasing streamwater DOC in summer, presumably owing to reduction processes in wetlands that mitigated the effects of acid deposition. Apparently, these reduction processes also produced small amounts of dissolved, non-ionic organic sulfur. Non-marine Ca^{2+} was related strongly to the percentage of upland hardwood forests in the catchments. Wetlands exert a profound influence on the chemistry of streams, principally through their export of DOC but also because of reduction reactions in their anoxic peats.

STEADY-STATE MODELS FOR CALCULATING CRITICAL LOADS OF ACIDITY FOR SURFACE WATERS

ARNE HENRIKSEN¹ and MAXIMILIAN POSCH²

¹ Norwegian Institute for Water Research (NIVA), Oslo, Norway; ² National Institute of Public Health and the Environment (RIVM), Bilthoven, The Netherlands
(e-mails: arne.henriksen@niva.no; max.posch@rivm.nl)

Abstract. Three models for calculating critical loads of acidity for surface waters, which have been used in several European countries to map regions sensitive to deposition of acidifying sulfur and nitrogen, are derived and their latest modifications are presented. Using Norwegian lake data as an example, some of the methods are compared and discussed. While the Steady-State Water Chemistry (SSWC) model and the Empirical Diatom model are based on water chemistry alone, the First-order Acidity Balance (FAB) model also includes descriptions of the most important sinks of nitrogen (and sulfur) in the catchment soils and the lake/sediment system. This is the first time that all currently used models as well as some new developments for calculating critical loads of acidity for surface waters are presented in a single paper.



Water, Air, and Soil Pollution: Focus 1: 375–398, 2001.

© 2001 Kluwer Academic Publishers. Printed in the Netherlands.

Critical loads of acidity for surface waters in south-central Ontario, Canada: regional application of the Steady-State Water Chemistry (SSWC) model

A. Henriksen, P.J. Dillon, and J. Aherne

1001 14 001

Abstract: Critical loads of acidity and the amount by which these critical loads are exceeded by atmospheric deposition (termed "exceedances") were estimated for 1469 lakes from five regions in south-central Ontario, Canada, using single lake chemistry measurements and sulphur deposition data for the period 1976–1999. Based on the Steady-State Water Chemistry (SSWC) model, four of the five regions had low critical loads, which is consistent with the underlying geology (silicate bedrock) and the thin glacial soils in these regions. Sulphur deposition in the study area showed a clear downward trend over the time period, with a decrease of approximately 50% to current levels of approximately $44 \text{ meq} \cdot \text{m}^{-2} \cdot \text{year}^{-1}$. As a result of the declining deposition, the portion of lakes with critical load exceedances has dropped substantially, from 74–82% in the four sensitive regions in 1976 to 11–26% in 1999. The pentile critical load is typically used as a regional target to account for uncertainties, but also to ensure that a sufficient percentage of lakes are protected (95%). This suggests that further reductions in emissions are required to reduce depositions to approximately $34 \text{ meq} \cdot \text{m}^{-2} \cdot \text{year}^{-1}$ ($11 \text{ kg S} \cdot \text{ha}^{-1} \cdot \text{year}^{-1}$) to prevent critical load exceedance.

Can. J. Fish. Aquat. Sci. 59: 1287–1295 (2002)

Factors affecting acid neutralizing capacity in the Adirondack region of New York: A solute mass balance approach

Ito M, Mitchell MJ, Driscoll CT, Roy KM

ENVIRONMENTAL SCIENCE & TECHNOLOGY 39 (11): 4076-4081 JUN 1 2005

Abstract: High rates of acidic deposition in the Adirondack region of New York have accelerated acidification of soils and surface waters. Annual input-output budgets for major solutes and acid-neutralizing capacity (ANC) were estimated for 43 drainage lake-watersheds in the Adirondacks from 1998 to 2000. Sulfate was the predominant anion on an equivalent basis in both precipitation and drainage export. Calcium ion had the largest cation drainage export, followed by Mg^{2+} . While these watersheds showed net nitrogen (N) retention, the drainage losses of SO_4^{2-} , Cl^- , base cations, and ANC exceeded their respective inputs from precipitation. Land cover (forest type and wetlands) affected the export of SO_4^{2-} , N solutes, and dissolved organic carbon (DOC). The relationships of solute export with elevation (negative for base cations and Cl^- , positive for NO_3^- and H^+) suggest the importance of the concomitant changes of biotic and abiotic watershed characteristics associated with elevational gradients. The surface water ANC increased with the sum of base cations and was greatest in the lakes with watersheds characterized by thick deposits of glacial till. The surface water ANC was also higher in the lake-watersheds with lower DOC export. Some variation in lake ANC was associated with variability in acidic deposition. Using a classification system previously developed for Adirondack lakes on the basis primarily of surficial geology, lake-watersheds were grouped into five classes. The calculated ANC fluxes based on the major sinks and sources of ANC were comparable with measured ANC for the thick-till (I) and the medium-till lake-watersheds with low DOC (II). The calculated ANC was overestimated for the medium-till with high DOC (III) and the thin-till with high DOC (V) lake-watersheds, suggesting the importance of naturally occurring organic acids as an ANC sink, which was not included in the calculations. The lower calculated estimates than the measured ANC for the thin-till lake-watersheds with low DOC (IV) were probably due to the mobilization of Al as an ANC source in these watersheds that were highly sensitive to strong acid inputs. Our analysis of various drainage lakes across the Adirondacks on the basis of solute mass balances, coupled with the use of a lake classification system and GIS data, demonstrates that the lake-watersheds characterized by shallow deposits of glacial till are highly sensitive to acidic deposition not only in the southwestern Adirondack region where previous field-based studies were intensively conducted but also across the entire Adirondack region. Moreover, the supply of organic acids and Al mobilization substantially modify the acid-base status of surface waters.

Acid Rain Effects on Aluminum Mobilization Clarified by Inclusion of Strong Organic Acids

G. B. LAWRENCE, *, † J. W. SUTHERLAND, ‡ C. W. BOYLEN, §
S. W. NIERZWICKI-BAUER, § B. MOMEN, | B. P. BALDIGO, †
AND H. A. SIMONIN

Environ. Sci. & Technol. 39 (11): 4076-4081.

Abstract: Assessments of acidic deposition effects on aquatic ecosystems have often been hindered by complications from naturally occurring organic acidity. Measurements of pH and ANCG, the most commonly used indicators of chemical effects, can be substantially influenced by the presence of organic acids. Relationships between pH and inorganic Al, which is toxic to many forms of aquatic biota, are also altered by organic acids. However, when inorganic Al concentrations are plotted against ANC (the sum of Ca^{2+} , Mg^{2+} , Na^+ , and K^+ , minus SO_4^{2-} , NO_3^- , and Cl^-), a distinct threshold for Al mobilization becomes apparent. If the concentration of strong organic anions is included as a negative component of ANC, the threshold occurs at an ANC value of approximately zero, the value expected from theoretical charge balance constraints. This adjusted ANC is termed the base-cation surplus. The threshold relationship between the base-cation surplus and Al was shown with data from approximately 200 streams in the Adirondack region of New York, during periods with low and high dissolved organic carbon concentrations, and for an additional stream from the Catskill region of New York. These results indicate that (1) strong organic anions can contribute to the mobilization of inorganic Al in combination with SO_4^{2-} and NO_3^- , and (2) the presence of inorganic Al in surface waters is an unambiguous indication of acidic deposition effects.

Metals in Scandinavian Surface Waters: Effects of Acidification, Liming, and Potential Reacidification

Espen Lydersen a; Stefan Löfgren b; Rolf Tore Arnesen a

a Norwegian Institute for Water Research.

b Swedish University of Agricultural Sciences, SLU.

Crit. Rev. Environ. Sci. Technol. 32(2&3):73-295.

ABSTRACT: This article is a state-of-the-art review about such metals as Al, Fe, Mn, Cu, Zn, Cd, Pb, Cr, Ni, Hg, and As in surface waters. It focuses on natural and anthropogenic sources, chemical properties and levels, and toxicity mechanisms of these metals to aquatic organisms, primarily fish and invertebrates. Organisms living in almost anoxic, sulfide-rich environments are not incorporated into this study. This information is then linked to a Nordic Lake Survey implemented in 1995 on major chemistry and metals in Scandinavian surface waters to scale the problems of metals in Swedish and Norwegian surface waters. Because many acidified Swedish and Norwegian lakes also are limed, we also assess the risk of remobilization of metals because these waters reacidify due to reduced liming activity. The concentrations and chemical properties of metals in lakes relative to the biological effect levels suggest that the potential risks associated to both current and potential reacidified status of limed waters decreases in the order $Al \gg Cd > Pb$ in Swedish and Norwegian lakes. Also Hg, because of the organometallic forms such as methylmercury (MeHg), might be of concern, because it biomagnifies in the food chain and subsequently of great importance for top predators, including human beings. However, other factors than pH, such as changes in organic matter load from the surrounding soils due to natural climatic variations, are much more important for the Hg load and thereby the Hg concentrations in lakes than pH. The risks associated with other metals such as Cu, Fe, Mn, Ni, and Zn are very low and have to be considered only occasionally, because high concentrations are very rare in Norwegian and Swedish lakes. Less than 2% of the lakes have concentrations \square the lowest biological risk levels quoted in the two countries. Because primarily As is present as anions in surface waters, this element differs significantly from the cationic metals. Only a few lakes have high As concentration in relation to critical levels in Sweden, and high As concentrations are mainly related to agricultural areas and consequently high pH waters.

INFLUENCE OF ORGANIC-ACIDS ON THE PH AND ACID-NEUTRALIZING CAPACITY OF ADIRONDACK LAKES

MUNSON RK, GHERINI SA

WATER RESOURCES RESEARCH 29 (4): 891-899 APR 1993

Abstract: Past approaches for evaluating the effects of organic acids on the acid-base characteristics of surface waters have typically treated them solely as weak acids. Analysis of data collected by the Adirondack Lakes Survey Corporation (ALSC) from 1469 lakes throughout the Adirondack region shows that this approach is not valid. While the data indicate that natural organics contain a continuum of acid functional groups, many of which display weak acid characteristics, a significant fraction of the organic acid is strong ($pK(a) < 3$). Dissolved organic carbon (DOC) contributes 4.5-5 $\mu\text{eq}/\text{mg}$ DOC of strong acid to solution. The associated anions make a negative contribution to Gran acid-neutralizing capacity (ANC). Because organic anions can produce negative Gran ANC values, the common practice of considering negative values of Gran ANC evidence of acidification solely by mineral acids is not valid. The strength of organic acids also influences the observed deviation between Gran ANC values and ANC values calculated as the difference between base cation and mineral acid anion concentrations ($C(B) - C(A)$). Ninety percent of the deviation is due to the presence of strong organics while the remaining 10% is due to DOC-induced curvature in the F1 Gran function. Organic acids can also strongly influence pH. Their largest effects were found in the 0-50 $\mu\text{eq}/\text{L}$ Gran ANC range where they depressed pH by up to 1.5 units. In addition, a method for predicting changes in pH in response to changes in mineral acidity, DOC, or both without having to rely on inferred thermodynamic constants and the uncertainties associated with them has been developed. Using the predictive method, the response of representative lakes from four sensitive lake classes to a 15- $\mu\text{eq}/\text{L}$ decrease in mineral acidity ranged from +0.17 to +0.38 pH units. If concurrent increases in DOC are considered, the pH changes would be even smaller.

Limnol. Oceanogr., 47(2), 2002, 333-342
© 2002, by the American Society of Limnology and Oceanography, Inc.

Synchronous variation of dissolved organic carbon and color in lakes

Michael L. Pace and Jonathan J. Cole

Institute of Ecosystem Studies, P.O. Box AB, Millbrook, New York 12545

Abstract

Temporal variation in dissolved organic carbon (DOC) and water color (light absorption at 440 nm) was measured in 20 lakes in northern Michigan that varied in DOC, pH, morphometry, and relative productivity as indicated by chlorophyll and total phosphorus (TP). Monthly observations during May–August over 6 yr revealed that DOC and color varied by 6- and 28-fold among lakes and varied substantially through time within lakes. The pattern of temporal variation differed among years but was synchronous among lakes. Of the 190 possible correlations among lake time series, most were positive for DOC (158) and color (160), and 50% of the positive correlations were significant ($P < 0.05$). Other variables, such as total phosphorus, chlorophyll, and pH, were less synchronous and had fewer significant positive correlations (13–25%). Temporal dynamics in DOC and color were related to ice-out date as well as spring and summer precipitation. Years of late ice-out and high spring rain were associated with high DOC and color in spring. A summer drought in one year led to declines in color (up to 40%) and DOC (up to 38%) in nearly all of the lakes. The common temporal dynamics of DOC and color were most likely the result of climatic conditions that affected loading of allochthonous carbon as well as losses due to photodegradation. The variations in DOC were sufficient to cause large changes in light penetration, standing stocks of carbon, and ecosystem metabolism.

Landscape influences on aluminum and dissolved organic carbon in streams draining the Hubbard Brook valley, New Hampshire, USA

Palmer SM, Wellington BI, Johnson CE, Driscoll CT

HYDROLOGICAL PROCESSES 19 (9): 1751-1769 JUN 15 2005

Abstract: Concentrations of both aluminum (Al) and dissolved organic carbon (DOC) in stream waters are likely to be regulated by factors that influence water flowpaths and residence times, and by the nature of the soil horizons through which waters flow. In order to investigate landscape-scale spatial patterns in streamwater Al and DOC, we sampled seven streams draining the Hubbard Brook valley in central New Hampshire. We observed considerable variation in stream chemistry both within and between headwater watersheds. Across the valley, concentrations of total monomeric aluminum (Al) ranged from below detection limits ($< 0.7 \mu\text{mol l}^{-1}$) to $22.3 \mu\text{mol l}^{-1}$. In general, concentrations of Al-m decreased as pH increased downslope. There was a strong relationship between organic monomeric aluminum (Al-O) and DOC concentrations ($R^2 = 0.92$).

We observed the highest Al concentrations in: (i) a watershed characterized by a steep narrow drainage basin and shallow soils and (ii) a watershed characterized by exceptionally deep forest floor soils and high concentrations of DOC. Forest floor depth and drainage area together explained much of the variation in $\ln \text{Al-m}$ ($R^2 = 0.79$; $N = 45$) and $\ln \text{DOC}$ ($R^2 = 0.87$; $N = 45$). Linear regression models were moderately successful in predicting $\ln \text{Al-m}$ and $\ln \text{DOC}$ in streams that were not included in model building. However, when back-transformed, predicted DOC concentrations were as much as 72% adrift from observed DOC concentrations and Al-m concentrations were up to 51% off. This geographic approach to modelling Al and DOC is useful for general prediction, but for more detailed predictions, process-level biogeochemical models are required.

DIATOM COMMUNITY DYNAMICS IN STREAMS OF CHRONIC AND EPISODIC ACIDIFICATION: THE ROLES OF ENVIRONMENT AND TIME

S. Passey (2006) *Journal of Phycology* 42 (2), 312–323.

Abstract: Community dynamics of epiphytic diatoms were studied for 3 years in a chronically and an episodically acidified tributary of Buck Creek, Adirondacks. Both streams experienced pulses of acidity during hydrologic events but these pulses were more pronounced in the episodically acidified stream, where pH decreased over two units (between 4.53 and 6.62) and the acid-neutralizing capacity (ANC) became negative. In the chronically acidified stream, pH was below 4.9 and the ANC was negative 94% of the time. In this stream, high inorganic acidity following SO_4^{2-} enrichment from snowmelt or rainstorms alternated with high organic acidity derived from a headwaters wetland during base flow. The fluctuating water chemistry generated shifts in diatom community composition: from exclusive dominance of *Eunotia bilunaris* (Ehrenberg) Mills during periods of high inorganic acidity to proliferation of several subdominant species during periods of high organic acidity. In the episodically acidified stream, the pulses of acidity were associated with high NO_3^- concentrations and the corresponding high ratios of inorganic monomeric Al (Al_{im}) to organic monomeric Al (Al_{om}). Diatom communities there were dominated exclusively by *E. exigua* (Brébisson) Rabenhorst year round; however, this species peaked during periods of low acidity. Periods of high acidity and $\text{Al}_{\text{im}}:\text{Al}_{\text{om}}$ ratios were marked by a decline in *E. exigua* and a concomitant increase in the subdominant species. Variance partitioning into terms of environmental and temporal variance, and their covariance, suggested that diatom communities in the chronically acidic stream were governed primarily by environmental factors while in the episodically acidic stream environmental and temporal factors had equal contributions.

Soil aluminum distribution in the near-stream zone at the Bear Brook Watershed in Maine Pellerin BA, Fernandez IJ, Norton SA, Kahl JS. WATER AIR AND SOIL POLLUTION 134 (1-4): 189-204 FEB 2002

Abstract: Near-stream and upslope soil chemical properties were analyzed to infer linkages between soil and surface water chemistry at the Bear Brook Watershed in Maine [BBWM]. Organic and mineral soil samples were collected along six 20 m transects perpendicular to the stream and one 200 m transect parallel to the stream. O horizon soils immediately adjacent to the stream had a significantly higher pH (4.20) and lower soil organic matter percentage (54%) than upslope O horizons (3.84 and 76%, respectively). Additionally, near-stream O horizon soils had significantly higher concentrations of water-soluble Al (2.7 x), exchangeable Al (2.3 x), and organically-bound Al (3.9 x) and significantly lower concentrations of exchangeable Ca (0.4 x) than O horizons upslope. These results suggest that Al can accumulate in non-hydric near-stream zone soils at this site. Mobilization of labile Al from near-stream zone soils during hydrologic events could play a key role in explaining controls on Al in stream water at BBWM.

Aluminum speciation in environmental samples: a review

Janez Ščančar . Radmila Milačič.
Anal Bioanal Chem. 386:999-1012.

Abstract

Because of its toxic effects on living beings, Al may represent an environmental hazard, particularly under increased acidic conditions. Growing environmental concern over the presence of increased Al concentrations in soil solutions and fresh waters resulted in the development of numerous analytical techniques for the determination of Al species. Al has a very complex chemistry that is significantly influenced by pH. Different Al species are present in environmental solutions, and many of them are unstable. Contamination of samples and reagents by extraneous Al represents an additional problem in speciation of Al at trace concentrations. Due to these reasons quantitative determination of particular chemical forms of Al is still a very difficult task for analytical chemists. The most important analytical methodologies of the last decade and new trends for the speciation of Al in environmental samples are comprehensively reviewed here.

Effects of Acid Rain on Freshwater Ecosystems

D. W. SCHINDLER 1988. *Science* 239 (4836)149-157

Acid-vulnerable areas are more numerous and widespread than believed 7 years ago. Lakes and streams in acid-vulnerable areas of northeastern North America have suffered substantial declines in acid-neutralizing capacity, the worst cases resulting in biological damage. Many invertebrates are very sensitive to acidification, with some disappearing at pH values as high as 6.0. However, the recent rate of acidification of lakes is slower than once predicted, in part the result of decreases in sulfur oxide emissions. A discussion of some of the processes that have contributed to the acidification of lakes as well as those that have protected acid-sensitive freshwaters is presented. The author is in the Department of Fisheries and Oceans, Freshwater Institute, 501 University Crescent, Winnipeg, Manitoba R3T 2N6, Canada.

Episodic Acidification of Small Streams in the Northeastern United States: Ionic Controls of Episodes

P. J. Wigington, Jr.; D. R. DeWalle; P. S. Murdoch; W. A. Kretser; H. A. Simonin; J. Van Sickle; J. P. Baker.

Ecological Applications, Vol. 6, No. 2. (May, 1996), pp. 389-407.

Abstract. As part of the Episodic Response Project (ERP), we intensively monitored discharge and stream chemistry of 13 streams located in the Northern Appalachian region of Pennsylvania and in the Catskill and Adirondack Mountains of New York from fall 1988 to spring 1990. The ERP clearly documented the occurrence of acidic episodes with minimum episodic $\text{pH} \leq 5$ and inorganic monomeric Al (Al_{im}) concentrations $>150 \mu\text{g/L}$ in at least two study streams in each region. Several streams consistently experienced episodes with maximum Al_{im} concentrations $>350 \mu\text{g/L}$. Acid neutralizing capacity (ANC) depressions resulted from complex interactions of multiple ions. Base cation decreases often made the most important contributions to ANC depressions during episodes. Organic acid pulses were also important contributors to ANC depressions in the Adirondack streams, and to a lesser extent, in the Catskill and Pennsylvania streams. Nitrate concentrations were low in the Pennsylvania streams, whereas the Catskill and Adirondack study streams had high NO_3^- concentrations and large episodic pulses ($\leq 54 \mu\text{eq/L}$). Most of the Pennsylvania study streams also frequently experienced episodic pulses of SO_4^{2-} ($\leq 78 \mu\text{eq/L}$), whereas the Adirondack and Catskill streams did not. High baseline concentrations of SO_4^{2-} (all three study areas) and NO_3^- (Adirondacks and Catskills) reduced episodic minimum ANC, even when these ions did not change during episodes. The ion changes that controlled the most severe episodes (lowest minimum episodic ANC) differed from the ion changes most important to smaller, more frequent episodes. Pulses of NO_3^- (Catskills and Adirondacks), SO_4^{2-} (Pennsylvania), or organic acids became more important during major episodes. Overall, the behavior of streamwater SO_4^{2-} and NO_3^- is an indicator that acidic deposition has contributed to the severity of episodes in the study streams.

Title: Solutes and soil in and around an in-stream wetland on the Hubbard Brook Experimental Forest, New Hampshire, USA Yavitt JB, Fahey TJ, Long R, Driscoll CT
WETLANDS 26 (2): 376-384 JUN 2006.

Abstract: We characterized soil and the concentrations of solutes in soil solutions and in stream water in and around a wetland located within a first-order stream in a forested watershed at the Hubbard Brook Experimental Forest (New Hampshire, USA). We hypothesized that the in-stream wetland would retain solutes in stream water, especially Ca^{2+} , H^+ , and strong acid anions (NO_3^- , SO_4^{2-}). Rather, the wetland had subtle impact on stream water chemistry causing slightly greater Na^+ concentrations and lesser concentrations of H^+ and dissolved inorganic C (DIC). We expected anaerobic microbial denitrification and SO_4^{2-} reduction in wetland soils to consume the strong acid anions and account for less H^+ , but Na^+ release was responsible. The wetland soil produced dissolved organic C (DOC) but did not export it into stream water. The DOC was saturated with monomeric Al, suggesting a sink rather than source for Al. Soil extracted with 1 M NH_4Cl yielded much larger amounts of Ca^{2+} and Mg^{2+} than in the surrounding mineral forest soil, whereas NH_4^+ , K^+ , and Na^+ budgets were smaller in the wetland soil than in the forest soil. Characterization of soil surface charge and organic matter fractions revealed distinct differences between wetland soil organic matter (SOM) and forest soil SOM. Our results suggest that the wetland behaves much like gelatin: the organic matrix holds water tightly, such that stream water flows mostly over the matrix rather than entering and forcing much of the old water into runoff. The subtle biogeochemical role of the wetland adds to the complex interactions that control solute mobility in small watersheds. Author Keywords: biogeochemistry; headwater wetland; organic matter; soil; stream water; subsurface water.

References (books, reports, conference proceedings) for which abstracts were not obtained include:

- Adams, M., DeWalle, D., and J. Hom, Eds. 2006. The Fernow Watershed Acidification Study. Environmental Pollution Vol. 11. Springer, New York.
- Kahl, J., Stoddard, J., Haeuber, R., Paulsen, S., Birnbaum, R., Deviney, F., Webb, J., DeWalle, D., Sharpe, W., Driscoll, C., Herlihy, A., Kellogg, J., Murdoch, P., Roy, K., Webster, K., and N. Urquhart. 2004. Have U.S. Surface Waters Responded to the 1990 Clean Air Act Amendments? *Environ. Sci. Technol.* 38:484A-490A.
- New Hampshire Department of Environmental Services. 2004. *Total Maximum Daily Load (TMDL) for 65 Acid Impaired New Hampshire Ponds. Final Report.* NHDES, Concord, NH.
- National Oceanic and Atmospheric Administration (NOAA) and Maine Atlantic Salmon Commission (MASC). 2006. Effects of low pH and High aluminum on Atlantic salmon smolts in Eastern Maine and liming project feasibility analysis. U.S. Atlantic Salmon Assessment Committee Working Paper. 27 pp.
- Sparling, D. and T. Lowe. 1996. Environmental hazards of aluminum to plants, invertebrates, fish, and wildlife. *Res. Environ. Contam. Toxicol.* 145:1-127.
- United States Environmental Protection Agency. 2003. Responses of surface water chemistry to the Clean Air Act Amendments of 1990. EPA-620/R-03/001.
- Yokel RA (2004) In: Merian E., Anke, M., Ihnat, M., and M Stoeppler, (eds). Aluminum: elements and their compounds in the environment. Occurrence, analysis and biological relevance. Vol. 2. Wiley-VCH, Weinheim, Germany.